

PRE-DILUTED COOLANT**TECHNICAL FIELD**

This invention generally relates to a pre-diluted coolant for direct use in internal-combustion engine systems, which requires no dilution with water. More particularly, this invention relates to a pre-diluted coolant that can excellently inhibit metal corrosion and scale formation in cooling systems and improve lubrication of mechanical seals of water pumps.

BACKGROUND ART

Conventionally, cooling systems of internal-combustion engines utilize coolants which are prepared by diluting glycol-based or alcohol-based coolant compositions with conventional water. It is known that a conventional cooling system which comprises various metallic parts such as aluminum, aluminum alloy, cast iron, steel, brass, solder and copper parts suffers from metal corrosion, chiefly through contact with water and air contained in the coolant flowing through the cooling system. It is also known that water conventionally used to dilute coolant compositions generally contains, among other substances or hard water elements, ions such as chlorine ions, sulfuric acid ions and bicarbonate ions which are known to be metal corrosive ions. These metal corrosive ions accelerate metal corrosion, especially under high temperature and pressure environments such as in cooling systems.

In order to inhibit metal corrosions in cooling systems, it is conventional to selectively blend in coolant

compositions metal corrosion inhibitors such as phosphates, amine salts, silicates, borates, nitrites and dibasic acids.

However, blending of such additives would raise additional problems. Phosphates tend to cause eutrophication in rivers or ponds when coolants containing phosphates are disposed of into rivers or ponds, which would increase BOD and COD in the waters. Increased BOD or COD would propagate algae, which are known to generate harmful red tides or become slimes that are to be accumulated on the riverbeds or pond beds.

Amine salts and nitrites when they coexist in coolants would chemically react with each other and produce nitrosoamine which is known to be a carcinogenic compound, while silicates are generally unstable in coolants and would easily gel when the temperature of the coolants rapidly changes or the pH value of the coolants changes and/or other salts coexist, leading to degradation in metal corrosion inhibition.

Borates are apt to corrode aluminum or aluminum alloy while nitrites will quickly degrade in coolants and lose their expected property in the coolants.

Besides chlorine ions, sulfuric acid ions and bicarbonate ions, hard water element ions such as calcium ions and magnesium ions are often melted in diluting water. Calcium and magnesium ions are known to be scale forming ions. Phosphates or dibasic acids contained in coolant compositions would chemically react with calcium and magnesium ions

contained in diluting water and would form scales or precipitation in coolants.

Scales formed as such would seriously affect corrosion inhibition function of phosphoric acids or dibasic acids, might clog circulation passages of cooling systems and/or would lower heat transfer function of coolants at high-temperature sections or spots such as cylinder head portions and valves by adhering thereto and may eventually physically damage such portions as well.

When a coolant composition containing "large" quantity of foregoing metal corrosion inhibitors is used, following problems would occur. Water or glycol in coolants where those metal corrosion inhibitors are melted would locally evaporate in the vicinities of hot spots such as mechanical seals of water pumps, and locally lower solubility of metal corrosion inhibitors in the coolants, producing precipitation of the metal corrosion inhibitors, which would adhere to the mechanical seals and eventually damage the sealing property of the mechanical seals.

The inventors of the present invention aimed at solving such water-related problems and have arrived at the present invention. Accordingly, it is a chief object of the present invention to provide a pre-diluted coolant that does not require dilution with water and thus is capable of effectively inhibiting metal corrosions and scale forming as well as improving lubrication of mechanical seals of water pumps altogether without suffering negative aspects of conventional

coolant compositions. Other objects of the present invention will become apparent from the descriptions that follow.

SUMMARY OF THE INVENTION

A pre-diluted coolant of the present invention which does not require later dilution with water can be directly used in the cooling system of an internal-combustion engine. The pre-diluted coolant of the present invention is characterized in that its chief component is deionized water where metal corrosive ions and scale forming ions are removed, or ethylene glycol aqueous solution prepared using such deionized water, or propylene glycol aqueous solution also prepared using such deionized water.

The term "deionized water" as used herein means water containing practically no metal corrosive ions such as chlorine ions, sulfuric acid ions and bicarbonate ions or scale forming ions such as calcium ions and magnesium ions. Such deionized water may be pure water or its practical equivalent. Such pure water may be aqueous electrolytic solution with specific resistance $10 \times 10,000 \Omega \cdot \text{cm}$ or over prepared, e.g., by utilizing an ion-exchange resin, or may be nuclear reactor water having specific resistance $100 \times 10,000 \Omega \cdot \text{cm}$ or over.

Since such deionized water (metal corrosive ions and scale forming ions are removed) is pre-blended in the pre-diluted coolant of the present invention, negative aspects that would otherwise be caused by the ions in the coolant can be effectively avoided. In addition, it has become possible

or feasible to substantially reduce contents of conventional metal corrosion inhibitors in coolants since progress of possible metal corrosions in cooling systems would be sufficiently slowed or inhibited by utilization of deionized water without relying much on metal corrosion inhibitors.

Local evaporation of water or glycols in the vicinities of mechanical seals would not seriously or materially affect the physical feature of the seals, because precipitation of metal corrosion inhibitors would effectively be prevented due to their limited use as will be readily appreciated by people skilled in the related art.

Further, as the pre-diluted coolant of the present invention does not practically contain scale forming ions and contains only minimum amounts of metal corrosion inhibitors, scale formation through chemical reaction between scale forming ions and certain metal corrosion inhibitors such as phosphoric acids and dibasic acids would be effectively inhibited, preventing scale precipitation and accumulation in the coolant.

The pre-diluted coolant according to the present invention selectively contains in an effective amount or amounts at least one metal corrosion inhibitor selected from alkali metal salts and amine salts of phosphoric acids, benzoic acid and alkali metal salts, ammonium salts and amine salts thereof, alkylbenzoic acids having a chemical structure $R-C_6H_4-COOH$ (R is a C1-C5 alkyl group) and alkali metal salts, ammonium salts and amine salts thereof, alkoxybenzoic acids

having a chemical structure $RO-C_6H_4-COOH$ (R is a C1-C5 alkyl group) and alkali metal salts, ammonium salts and amine salts thereof, cinnamic acids, alkylcinnamic acids and alkoxycinnamic acids having a chemical structure $R-C_6H_4-CH=CHCOOH$ (R is a C1-C5 alkyl or alkoxy group) and alkali metal salts, ammonium salts and amine salts thereof, other aromatic carboxylates, C6-C12 aliphatic monobasic acids and C6-C12 aliphatic dibasic acids and their alkali metal salts, ammonium salts and amine salts, other aliphatic carboxylates, aromatic polyvalent carboxylic acids, molybdates, tungstates, vanadates, alkali metal salts of nitric acid, alkali metal salts of silicic acids, alkali metal salts of boric acids, alkali metal salts of nitrous acid, triazole hydrogencarbonate, mercaptobenzothiazole, strontium compounds, 2-phosphonobutane-1,2,4 tricarboxylic acid and alkali metal salts thereof.

BRIEF DESCRIPTION OF THE DRAWING

FIG.1 is a schematic view of a mechanical seal leakage unit test system.

EMBODIMENT/COMPARISON TESTING

A number of test samples were prepared and named Embodiments ("Emb." for short) 1-7 and Comparisons ("Com." for short) 1-7 as provided in Table I. Ethylene glycol and water were respectively mixed in the indicated weight ratios, where the indicated percentages by weight of the additives were respectively blended. Metal corrosion tests were carried out using these samples in accordance with

JIS2234-1994. II (an officially recognized Japanese test standard). Tables II-1 and II-2 show the metal corrosion test results and evaluations. The deionized (good) water used to prepare Embodiments 1-7 was ion-exchange water or distilled water with ion concentrations of chlorine 10mg/litter or lower and sulfuric acid 10mg/litter or lower, with hardness (measured in CaCO₃) 20mg/litter or lower.

Bad water (1) was tap water, having ion concentrations of chlorine 49mg/litter and sulfuric acid 38mg/litter with hardness (CaCO₃) 89mg/litter. Badwater (2) was ionized water containing sodium sulfate 148mg/litter, sodium chloride 165mg/litter and sodium hydrocarbon 138mg/litter. Bad water (3) was ion exchange water containing calcium chloride 275mg/litter, sodium sulfate 148mg/litter, sodium chloride 165mg/litter and sodium hydrocarbon 138mg/litter.

TABLE I

Ingredient	Emb. 1	Com. 1-1	Com. 1-2	Emb. 2	Com. 2	Emb. 3	Com. 3	Emb. 4
Ethylene Glycol	15	15	15	50	50	30	30	15
Deionized Water	85	0	0	50	0	70	0	85
Bad Water (1)	0	85	0	0	0	0	0	0
Bad Water (2)	0	0	85	0	0	0	70	0
Bad Water	0	0	0	0	50	0	0	0

(3)								
Potassium Hydroxide	0.17	0.17	0.17	0.55	0.55	0.11	0.11	0.055
Ortho-Phosphoric Acid	0.17	0.17	0.17	0.55	0.55	0.11	0.11	0.055
Sodium Hydroxide	0	0	0	0	0	0	0	0
Sodium Benzoate	0.45	0.45	0.45	1.5	1.5	0.3	0.3	0.15
P-tert Butyl Benzoic Acid	0	0	0	0	0	0	0	0
Sodium Molybdate	0.06	0.06	0.06	0.2	0.2	0.04	0.04	0.02
Sodium Mercapto-benzothiazole	0.03	0.03	0.03	0.1	0.1	0.02	0.02	0.01
Tolyltriazole	0.03	0.03	0.03	0.1	0.1	0.02	0.02	0.01
Benzotriazole	0	0	0	0	0	0	0	0
Sodium Nitrate	0.06	0.06	0.06	0.2	0.2	0.04	0.04	0.02
pH	7.4	7.4	7.4	7.6	7.6	7.5	7.5	7.4

Ingredient	Com.	Com.	Emb.	Com.	Emb.	Com.	Emb.	Com.
	4-1	4-2	5	5	6	6	7	7
Ethylene Glycol	15	15	15	15	30	30	15	15
Deionized Water	0	0	85	0	70	0	85	0

Bad Water	85	0	0	0	0	0	0	0
(1)								
Bad Water	0	85	0	85	0	70	0	85
(2)								
Bad Water	0	0	0	0	0	0	0	0
(3)								
Potassium	0.055	0.055	0	0	0	0	0	0
Hydroxide								
Ortho-	0.055	0.055	0	0	0	0	0	0
Phosphoric								
Acid								
Sodium	0	0	0.069	0.069	0.046	0.046	0.023	0.023
Hydroxide								
Sodium	0.15	0.15	0.15	0.15	0.1	0.1	0.05	0.05
Benzoate								
P-tert Butyl	0	0	0.3	0.3	0.2	0.2	0.1	0.1
Benzoic Acid								
Sodium	0.02	0.02	0	0	0	0	0	0
Molybdate								
Sodium	0.01	0.01	0	0	0	0	0	0
Mercapto-								
benzothiazole								
Tolyltriazole	0.01	0.01	0	0	0	0	0	0
Benzotriazole	0	0	0.045	0.045	0.03	0.03	0.015	0.015
Sodium	0.02	0.02	0.075	0.075	0.05	0.05	0.025	0.025
Nitrate								
pH	7.4	7.4	7.7	7.7	7.8	7.8	7.7	7.7

TABLE II-1

Change in Weight mg/cm ²					
	JIS	Emb.	Com.	Com.	Emb.
	K2234-1994	1	1-1	1-2	3
II					
Cast	±0.30	0.00	-0.15	-0.24	0.00
Aluminum					
Cast Iron	±0.15	+0.02	-0.14	-0.18	+0.05
Steel	±0.15	0.00	-0.04	-0.02	0.00
Brass	±0.15	0.00	-0.03	-0.04	0.00
Solder	±0.30	-0.10	-0.16	-0.20	-0.04
Copper	±0.15	-0.01	-0.04	-0.03	-0.01
Appearance	(5)	cast Fe cast Al/Fe			
		good	corroded	corroded	good
Foaming	(6)	good	good	good	good
(AFTER TEST)					
pH	6.5-11.0	7.1	7.2	7.2	7.1
Change in pH	±1.0	-0.3	-0.2	-0.2	-0.3
Change	report	-4	-5	-3	-2
in Alkalinity (%)					
Liquid Phase	(7)	good	good	good	good
Precipitation	≤0.5	<0.05	<0.05	<0.05	<0.05
(vol.%)					
Change in Weight mg/cm ²					
	JIS	Com.	Emb.	Com.	Com.
	K2234-1994	3	4	4-1	4-2
II					
Cast	±0.30	+0.02	-0.01	-0.88	-1.24
Aluminum					

Cast Iron	± 0.15	-0.09	+0.06	-0.18	-0.17
Steel	± 0.15	-0.02	+0.03	-0.03	-0.01
Brass	± 0.15	+0.01	0.00	-0.03	-0.02
Solder	± 0.30	-0.19	-0.08	-0.18	-0.22
Copper	± 0.15	0.00	-0.01	-0.04	-0.02
Appearance	(5)	cast		cast	cast
		Fe/solder		Al/Fe	Al/Fe/solder
		corroded	good	corroded	corroded
Foaming	(6)	good	good	good	good
(AFTER TEST)					
pH	6.5-11.0	7.2	7.2	7.4	7.4
Change in pH	± 1.0	-0.2	-0.2	0	0
Change	report	-8	-5	-6	-4
in Alkalinity (%)					
Liquid Phase	(7)	good	good	good	good
Precipitation	≤ 0.5	<0.05	<0.05	<0.05	<0.05
(vol.%)					

TABLE II-2

Change in Weight mg/cm2					
	JIS	Emb.	Com.	Emb.	Com.
	K2234-1994	5	5	6	6
II					
Cast	±0.30	-0.14	-0.52	-0.18	-0.48
Aluminum					
Cast Iron	±0.15	-0.01	-0.03	-0.05	-0.18
Steel	±0.15	0.00	-0.06	-0.05	-0.07
Brass	±0.15	-0.03	-0.04	-0.04	-0.05

Solder	± 0.30	-0.03	-0.07	-0.10	-0.02
Copper	± 0.15	-0.05	-0.05	-0.07	-0.06
Appearance	(5)		cast		cast
			Al		Al/Fe
		good	corroded	good	corroded
Foaming	(6)	good	good	good	good

(AFTER TEST)

pH	6.5-11.0	8.4	8.5	8.3	8.6
Change in pH	± 1.0	+0.3	+0.3	+0.1	+0.4
Change	report	+4	-8	-4	-2
	in Alkalinity (%)				
Liquid Phase	(7)	good	good	good	good
Precipitation	≤ 0.5	<0.05	<0.05	<0.05	<0.05
	(vol.%)				

JIS	Emb.	Com.
K2234-1994	7	7

II

Cast	± 0.30	-0.22	-0.77
Aluminum			
Cast Iron	± 0.15	-0.10	-0.35
Steel	± 0.15	-0.07	-0.11
Brass	± 0.15	-0.08	-0.03
Solder	± 0.30	-0.14	-0.03
Copper	± 0.15	-0.11	-0.07
Appearance	(5)		cast
			Al/Fe
		good	corroded
Foaming	(6)	good	good

(AFTER TEST)

pH	6.5-11.0	8.4	8.6
Change in pH	± 1.0	+0.2	+0.4
Change	report	-5	-8
in Alkalinity (%)			
Liquid Phase	(7)	good	good
Precipitation	≤ 0.5	<0.05	<0.05
(vol.%)			

In Tables II-1 and II-2, the numerals (5), (6) and (7) respectively signify the following.

Numeral (5) - There is no showing of corrosion except at the contacting portions between the test sample and spacer. Change in color is not questioned.

Numeral (6) - There is no showing of foam overflow.

Numeral (7) - There is no significant change in color. There is no significant phase separation or gelation.

Embodiment 2 and Comparison 2 were further subjected to both a mechanical seal leakage unit testing and stability testing in hard water. The test conditions are provided in Table III and the test system shown in Fig.1 was utilized. The test results are given in Table IV.

TABLE III

Mechanical Seal Leakage Unit Test Conditions

Concentration v/v%	50
Time h	200

Temperature °C 90
Revolution r.p.m. 6500
External Pressure kg/cm2 1.0

The stability test was conducted using 200ml test samples in glass beakers which had been left for 24 hours at room temperatures. The test samples were centrifuged under the JIS K 2503 test conditions (an official Japanese testing standard). Amounts of precipitation were then measured.

TABLE IV

	Embodiment 2	Comparison 2
Leakage ml	<1	18
Precipitation v/v%	0	1.2